

AD-A141 513

SYNTHESIS AND STRUCTURE OF SULFUR DERIVATIVES OF A
(METHYLENE)PHOSPHINE(U) TEXAS CHRISTIAN UNIV FORT WORTH
DEPT OF CHEMISTRY M CAIRA ET AL. 18 MAY 84

1/1

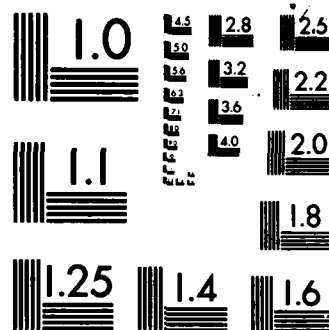
UNCLASSIFIED

TCU/DC/TR-84-03 N00014-79-C-0632

F/G 7/3

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

12

AD-A141 513

OFFICE OF NAVAL RESEARCH

Contract No. N00014-79-C-0632

Task No. NR-053-720

TECHNICAL REPORT NO. TCU/DC/TR-84-03

Synthesis and Structure of Sulfur Derivatives
of a (Methylene)phosphine

by

M. Caira, R.H. Neilson, W.H. Watson
P. Wisian-Neilson, Z.-M. Xie

Prepared for Publication

in

J. Chem. Soc., Chem. Commun.

Texas Christian University
Chemistry Department
Fort Worth, TX 76129

May 18, 1984

DTIC
ELECTE
MAY 30 1984
B

DTIC FILE COPY

Reproduction in whole or in part is
Permitted for any purpose of the United States Government

This document has been approved for public
release and sale; its distribution is unlimited

84 05 29 002

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TCU/DC/TR-84-03	2. GOVT ACCESSION NO. AD-A141501	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis and Structure of Sulfur Derivatives of a (Methylene)phosphine		5. TYPE OF REPORT & PERIOD COVERED Technical Report, 1983
		6. PERFORMING ORG. REPORT NUMBER TR-84-03
7. AUTHOR(s) M. Caira, R.H. Neilson, W. H. Watson P. Wisian-Neilson, Z.-M. Xie		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0632
9. PERFORMING ORGANIZATION NAME AND ADDRESS Texas Christian University Fort Worth, TX, 76129		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-053-720
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research		12. REPORT DATE May 18, 1984
		13. NUMBER OF PAGES 8
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Prepared for publication in <u>J. Chem. Soc., Chem. Commun.</u>		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) (Methylene)phosphine Thiaphosphirane Thioxophosphorane		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The methylenephosphine $\text{MesP}=\text{C}(\text{SiMe}_3)_2$ (1, Mes=mesityl) is smoothly oxidized by elemental sulfur to the 3-membered ring system $\text{MesP}(=\text{S})-\text{S}-\text{C}(\text{SiMe}_3)_2$ (3) which, upon treatment with $n\text{-Bu}_3\text{P}$, is converted to the 3-coordinate phosphorane $\text{MesP}(=\text{S})=\text{C}(\text{SiMe}_3)_2$ (2). The nearly isostructural nature of compounds 2 and 3 is confirmed by their X-ray crystallographic analyses.		

DD FORM 1473
1 JAN 73EDITION OF 1 NOV 63 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Synthesis and Structure of Sulfur Derivatives of a

Methylenephosphine

Mino Caira, Robert H. Neilson*, William H. Watson*,
Patty Wisian-Neilson, and Ze-Min Xie

Department of Chemistry, Texas Christian University
Fort Worth, Texas 76129 (USA)

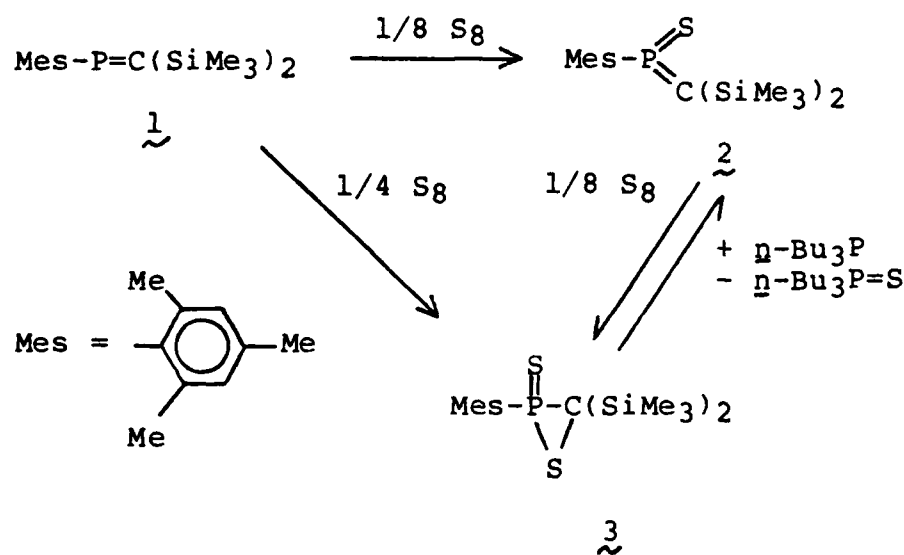
Summary. The methylenephosphine $\text{MesP}=\text{C}(\text{SiMe}_3)_2$ (1) (Mes = mesityl) is smoothly oxidized by elemental sulfur to the 3-membered ring system $\text{MesP}(=\text{S})-\text{S}-\text{C}(\text{SiMe}_3)_2$ (3) which, upon treatment with $n\text{-Bu}_3\text{P}$, is converted to the 3-coordinate phosphorane $\text{MesP}(=\text{S})=\text{C}(\text{SiMe}_3)_2$ (2). The nearly isostructural nature of compounds 2 and 3 is confirmed by their X-ray crystallographic analyses.

There has been considerable interest recently in π -bonded phosphorus compounds such as the methylenephosphines and their related oxidation products.^{1,2} We report here the synthesis and the crystal structure analyses of the products of the oxidation of mesityl[bis(trimethylsilyl)methylenephosphine, 1,³ by elemental sulfur.

Treatment of 1 with one equivalent of sulfur resulted in an inseparable mixture of the methylene(thioxo)phosphorane 2, the thiaphosphirane 3, and starting material 1. Addition of a second

list	special
A-1	

equivalent of sulfur afforded complete conversion of the mixture to 3. A pure sample of 2 was then obtained by the reaction of 3 with $n\text{-Bu}_3\text{P}$.



Compound 2 represents a stable analog to the proposed intermediate, $[(o\text{-Me})_2\text{C}_6\text{H}_3]\text{P}(=\text{S})=\text{CPh}_2$ ^{2b} (31_{P} δ 140.6)⁴, in the oxidation of methylenephosphines by sulfur. Stable, non-crystalline analogs of both 2 and 3, $\text{R}_2\text{N-P}(=\text{S})=\text{CHR}$ and $\text{R}_2\text{N-P}(=\text{S})-\text{S}-\text{CHR}$ ($\text{R} = \text{Me}_3\text{Si}$) have been prepared by Niecke and Wildbrecht^{2a} using a similar procedure. The crystal structures reported here are the first for the P-C-S three-membered ring system and one of the few⁵ reported for three-coordinate P(V) compounds.

The molecular structures of 2 and 3 are shown in perspective views in Figures 1 and 2, respectively. They are, in fact, nearly isostructural^{6,7} with twenty non-hydrogen atoms occupying

very similar positions but with no electron density at the S(2) position in 2. In compound 2, the P=C(10) distance lies just below the lower limit of the range of P=C distances reported for methylenephosphines,¹ 1.68–1.72 Å. The sums of the valence angles subtended by atoms P and C(10) are 359.9° and 359.8°, respectively, confirming sp² hybridization at these centers. In contrast, atoms P and C(10) in 3 are pyramidalized, lying 0.42 and 0.36 Å, respectively, above the plane of their four bonded atoms (coplanar to within 0.04 Å) in the direction of S(2).

Acknowledgment. The financial support of the U.S. Office of Naval Research, the Robert A. Welch Foundation, (P-074, P-759), the U. S. Army Research Office, and the C.S.I.R. (Pretoria) is gratefully acknowledged.

References

1. Appel, R.; Knoll, F.; Ruppert, I. Angew. Chem. Int. Ed. Engl. 1981, 20, 731.
2. See for example: (a) Niecke, E.; Wildbrecht, D.-A. J. Chem. Soc., Chem. Comm. 1981, 72. (b) Van der Knaap, T.A.; Klebach, T.C.; Lourens, R.; Vos, M.; Bickelhaupt, F. J. Am. Chem. Soc. 1983, 105, 4026. (c) Neilson, R.H. Inorg. Chem. 1981, 20, 1679.
3. Neilson, R.H.; Xie, Z.-M., manuscript in preparation.
4. Bickelhaupt, F., Reported at the International Conference on Phosphorus Chemistry, Nice, France, September, 1983.
5. (a) Pohl, S.; Krebs, B. Chem. Ber. 1977, 110, 3183. (b) Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. J. Chem. Soc., Chem. Commun. 1983, 862.
6. Crystal data for 2: a = 17.539(3), b = 13.393(2), c = 8.934(2) Å, V = 2077.1(7) Å³, orthorhombic, space group Pn2₁a (standard setting Pna2₁), ρ_c = 1.089 gcm⁻³ for Z = 4, μ(CuKα) = 3.02 mm⁻¹, F(000) = 736.0.

Crystal data for 3 : $a = 17.455(4)$, $b = 13.756(4)$, $c = 8.973(2)\text{\AA}$, $V = 2154.5(9)\text{\AA}^3$, orthorhombic, space group $Pn2_1a$, $\rho_c = 1.149\text{ gcm}^{-3}$ for $Z = 4$, $\mu(\text{CuK}\alpha) = 3.80\text{ mm}^{-1}$, $F(000) = 800.0$.

7. Intensity data for 2 and 3 were collected at 293K from spherically-ground crystals (average radii 0.133, 0.125mm) mounted on a Syntex P2₁ automatic diffractometer employing CuK radiation. The space group was deduced from systematic absences and intensity statistics. The structure of 3 was determined by direct methods. Similarity in morphology, cell dimensions and the common space group indicated close correspondence between the two molecular structures and their crystal packing. For 2, the positions of P, S(1), Si(1) and Si(2) of 3 were accordingly used to phase difference Fourier syntheses from which the remaining atoms of 2 were located. Both structures were refined by blocked-matrix least-squares methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. H atoms were included at geometrically constrained positions (C-H 1.08Å) based on those found in difference maps, with fixed isotropic thermal parameters equal to those of their parent atoms. Final R factors were $R = 0.061$, $R_w = 0.064$ for 2 (1209 unique reflexions) and $R = 0.045$, $R_w = 0.047$ for 3 (1269 unique reflexions). Since the space group is polar and anomalous dispersion corrections were applied to the S, P and Si scattering factors, it was necessary to test the absolute polarities of the crystals chosen for analysis. Significance tests based on Hamilton's R-ratio indicated that the crystals of 2 and 3 chosen had opposite polarity. The deposited fractional coordinates reflect this difference. Enantiomers of 2 and 3 with the same chirality are illustrated in the Figures to emphasize the similarity between the molecular structures.

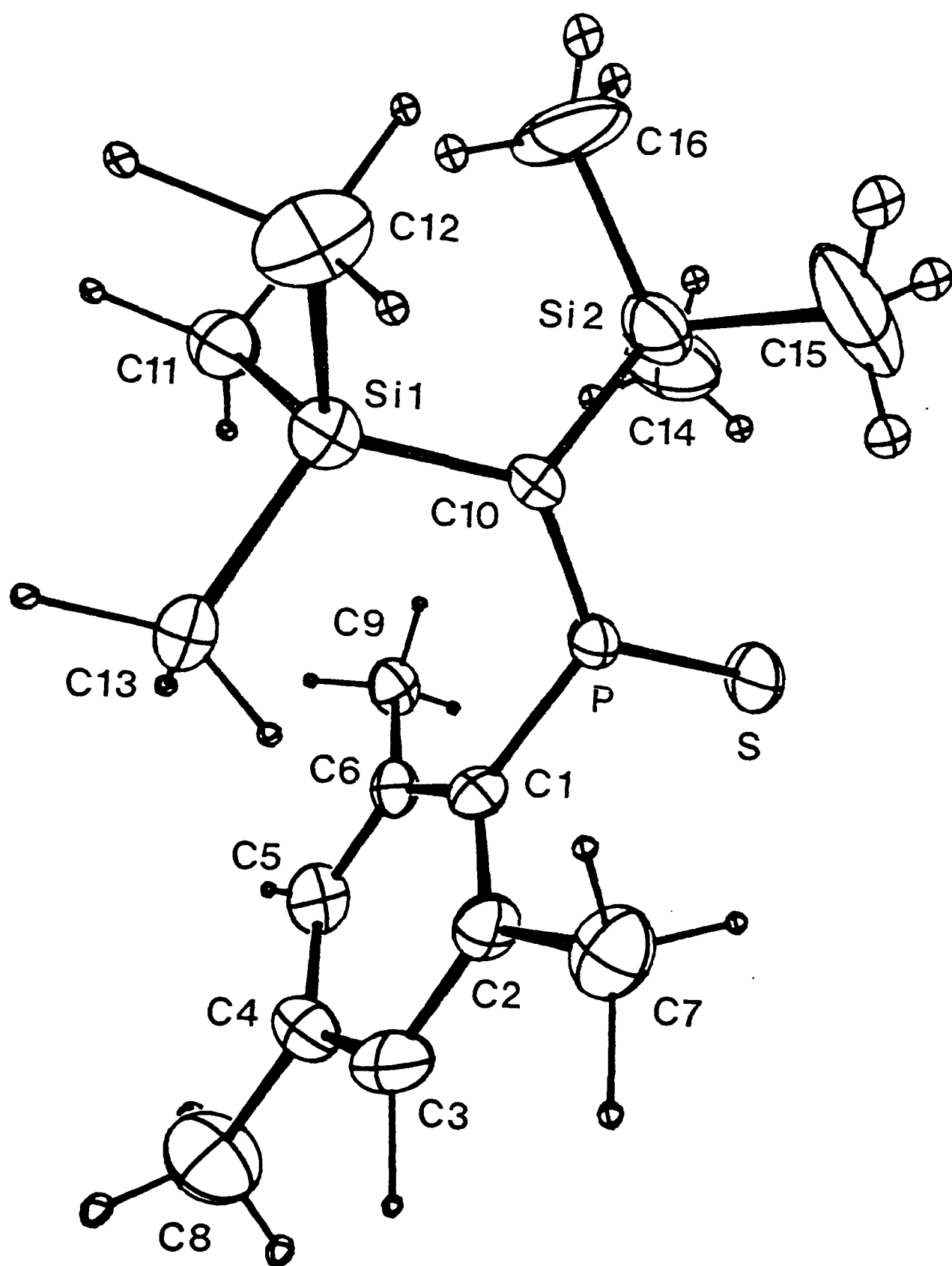
Table. NMR Spectroscopic Data ^{a,b}

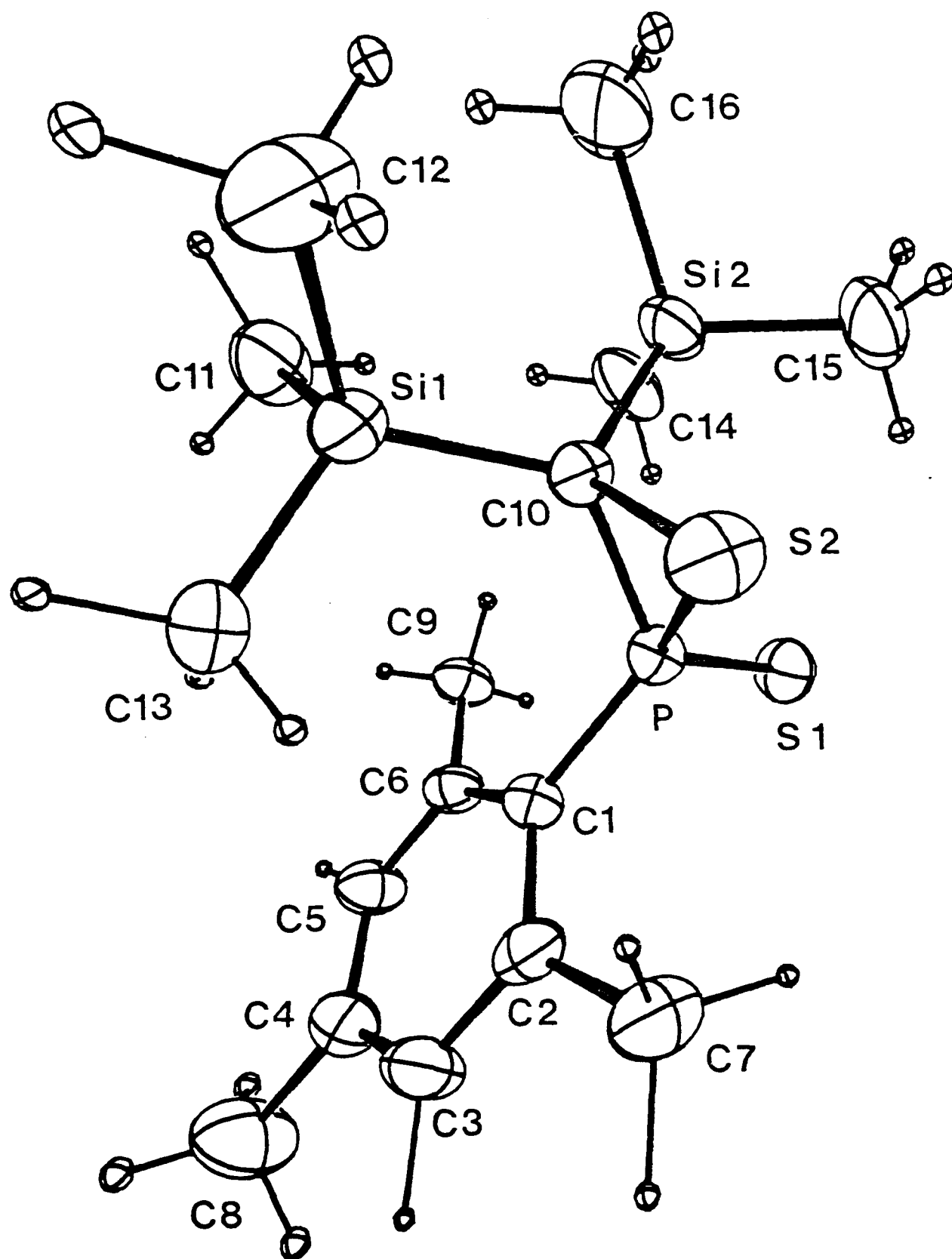
compd	signal	¹ H NMR		¹³ C NMR		³¹ P NMR
		δ	J _{PH}	δ	J _{PC}	δ
2	Me ₃ Si	-0.22		2.11		190.9
		0.39		2.56		
	P-C			126.00	34.2	
	o-Me	2.23		22.50	7.3	
	p-Me	2.51	1.5	21.48		
3	Me ₃ Si	-0.26		0.14	3.1	2.6
		0.38		1.66	3.4	
	P-C			26.39	8.6	
	o-Me ₂	2.66	1.5	22.76	4.3	
		2.57	1.1	22.19	5.5	
	p-Me	2.20		21.15	1.2	

^a Chemical shifts downfield from Me₄Si for ¹H and ¹³C and from H₃PO₄ for ³¹P spectra; coupling constants in Hz. Solvents: ¹H, CH₂Cl₂; ¹³C and ³¹P, CDCl₃. ^b Data for phenyl signals to be published.³ ₂ Non-equivalent o-Me groups due to hindered rotation about P-C(ring) bond.

Figure 1. Molecular structure of 2 : Mes-P(=S)=C(SiMe₃)₂. Principal bond lengths (angstrom) and angles (degrees) are: P=S 1.925(4), P=C(10) 1.647(9), P-C(1) 1.80(1), Si(1)-C(10) 1.88(1), Si(2)-C(10) 1.89(1), S-P-C(1) 113.1(3), S-P-C(10) 127.8(4), C(1)-P-C(10) 119.0(5), P-C(10)-Si(1) 123.8(6), P-C(10)-Si(2) 115.8(6), Si(1)-C(10)-Si(2) 120.2(5). Thermal ellipsoids in both figures drawn at the 35% probability level.

Figure 2. Molecular structure of 3 : Mes-P(=S)-S-C(SiMe₃)₂. Principal bond lengths (angstrom) and angles (degrees) are: P=S(1) 1.932(3), P-S(2) 2.049(3), P-C(10) 1.795(7), P-C(1) 1.793(7), S(2)-C(10) 1.918(8), Si(1)-C(10) 1.920(8), Si(2)-C(10) 1.918(7), S(1)-P-C(1) 112.7(2), S(1)-P-C(10) 123.2(3), C(1)-P-C(10) 116.3(3), P-C(10)-Si(1) 123.4(4), P-C(10)-Si(2) 115.8(4), Si(1)-C(10)-Si(2) 117.1(4), S(1)-P-S(2) 121.6(1), S(2)-P-C(1) 113.7(3), S(2)-P-C(10) 59.4(2), P-S(2)-C(10) 53.7(2), P-C(10)-S(2) 66.9(3), S(2)-C(10)-Si(1) 106.4(3), S(2)-C(10)-Si(2) 114.4(4).





END

FILMED

ADTIC